



Novel hydrophilic and hydrophobic double microporous layer coated gas diffusion layer to enhance performance of polymer electrolyte fuel cells under both low and high humidity

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HIGHLIGHTS

- Novel hydrophilic and hydrophobic double MPL coated GDL was developed.
- The hydrophilic layer coated on the hydrophobic MPL is effective to conserve MEA hydration under low humidity.
- The hydrophobic intermediate MPL prevents the removal of water in the hydrophilic layer.
- Appropriate double MPL is also effective to reduce flooding under high humidity.

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ABSTRACT

A novel hydrophilic and hydrophobic double microporous layer (MPL) coated gas diffusion layers (GDL) was developed to enhance the performance of polymer electrolyte fuel cells (PEFCs) under both low and high humidity. A thin hydrophilic layer using titanium dioxide (TiO₂) coated on the hydrophobic MPL is effective at conserving the humidity of the membrane electrode assembly (MEA) under low humidity, while a hydrophobic intermediate MPL between the hydrophilic layer and the carbon paper substrate prevents the removal of water from the hydrophilic layer. This results in a significant enhancement of PEFC performance under low humidity over that for a conventional hydrophobic MPL coated GDL.

The double MPL coated GDL is also effective at increasing the discharge of excess water from the catalyst layer, which reduces flooding and achieves further enhancement of the PEFC performance under high humidity, compared with that for a conventional hydrophobic MPL coated GDL. The appropriate pore diameter and hydrophobicity, and decrease in the thickness of the hydrophobic intermediate MPL in the double MPL, are essential to enhance the PEFC performance.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) with high efficiency and low environmental impact have been developed in recent years. However, further improvements in performance and reliability, as well as a reduction in production costs are required to ensure that PEFCs constitute a larger proportion of future power generation devices. PEFC systems generally have external humidifiers to supply humidified fuel and oxidant gases, preventing dehydration of the membrane electrode assembly (MEA). Loss of water content in

the membrane decreases ionic conductivity, which increases the internal resistance of the PEFC. A PEFC operated without the need for external humidifiers would realize a very simplified overall PEFC system with increased total efficiency and reduced cost. One of the most important issues to advance the commercial viability of PEFCs is to develop a high performance PEFC that can operate without humidification [1–7].

The design parameters of the gas diffusion layer (GDL), such as thickness, pore size, and the hydrophobic and hydrophilic properties, influence the water management characteristics during PEFC operation. Several investigations have demonstrated that a hydrophobic microporous layer (MPL) coated on a GDL substrate can effectively improve the water management characteristics, which enhances the PEFC performance [8–13]. An appropriate MPL coated GDL prevents dehydration of the MEA under low humidity

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and reduces flooding under high humidity. However, the appropriate design parameters of the MPL coated GDL are different under low and high humidity conditions [14]. An MPL coated GDL designed to enhance the ability to prevent MEA dehydration under low humidity is generally inferior in its ability to reduce flooding under high humidity. Even when a PEFC is operated without humidification, it is essential to prevent flooding due to water produced in the cell at high current densities. Therefore, it is important to develop a robust MPL coated GDL that enhances PEFC performance under both low and high humidity.

The authors have reported that a novel hydrophilic and hydrophobic double MPL coated GDL was developed to enhance the PEFC performance under low humidity over that for a conventional hydrophobic MPL coated GDL [15]. For the double MPL, it is expected that a thin hydrophilic layer using polyvinyl alcohol (PVA) coated on a hydrophobic MPL would be effective at conserving MEA hydration, and that a hydrophobic intermediate MPL between the hydrophilic layer and the carbon paper substrate would prevent the removal of water from the hydrophilic layer. In the present study, PEFC performance tests under both low and high humidity were conducted. Hydrophilic layers using either PVA or titanium dioxide (TiO_2) were coated on the hydrophobic MPL for the double MPL coated GDLs. The appropriate pore diameter, thickness, and the hydrophilic and hydrophobic properties of the double MPL coated GDL were clarified in order to prevent MEA dehydration under low humidity and to reduce flooding under high humidity.

2. Experimental

2.1. Tested GDLs

Fig. 1 shows the GDLs used at the anode and cathode. The GDL used at the anode was a commercial carbon paper without an MPL (SGL SIGRACET®24BA), which was treated with 5 mass% polytetrafluoroethylene (PTFE) loading to impart hydrophobicity. The SGL24BA GDL had a thickness of 190 μm , an areal weight of 54 g m^{-2} and 84% porosity. Hydrophobic MPL, and hydrophilic and hydrophobic double MPL coated GDLs were used at the cathode. The hydrophobic MPL coated GDL was a commercial GDL (SGL SIGRACET®24BC) with a thickness of 240 μm and an areal weight of 100 g m^{-2} . This was essentially the SGL24BA GDL coated with an MPL consisting of 20 mass% PTFE and carbon black [9]. For the double MPL coated GDLs, hydrophilic layers using either polyvinyl alcohol (PVA) or titanium dioxide (TiO_2) were coated on the hydrophobic MPL coated GDL [15]. The hydrophilic layers using PVA consist of 5 or 10 mass% PVA (Nippon Synthetic Chemical GOHSEFIMER®Z-100) and carbon black (Denki Kagaku Kogyo DENKA BLACK®HS-100). The hydrophilic layer using TiO_2 consists of 25 mass% TiO_2 (Sakai Chemical Industry STR-100A) as hygroscopic particles with an average size of 10 nm, 5 mass% silicone (Shin-Etsu Chemical KM-2002L) and carbon black (DENKA BLACK®HS-100).

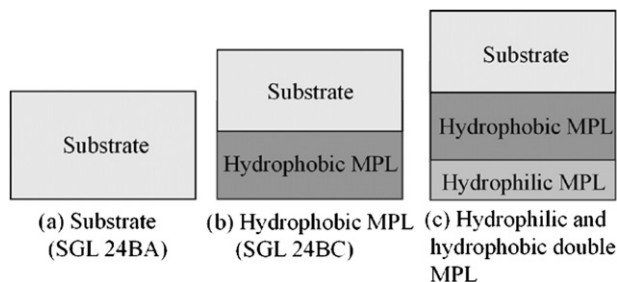


Fig. 1. GDLs used at the anode and cathode.

The hydrophobic intermediate MPL in the double MPL, which consists of PTFE (Daikin Polyflon D-210C) and carbon black (DENKA BLACK®HS-100), was coated on the carbon paper substrate as follows. A slurry containing PTFE, carbon black, distilled water and a surface-active agent was mixed using an impeller blade-type mixer, and then spread on the substrate using a bar coating machine. The MPL was dried in an oven and then heated at 350 $^{\circ}\text{C}$ to remove any remaining solvent and to sinter PTFE and carbon black onto the substrate. The PTFE content in the hydrophobic intermediate MPL was varied between 10 and 40 mass%.

2.2. GDL pore diameter, contact angle, and water vapor permeability measurements

Fig. 2 shows a schematic diagram of the test apparatus used to evaluate the air and water permeability of the GDL [14]. A 13 mm-diameter GDL, with a thickness of h , was placed between two cylindrical plates. The compressive force was controlled using a clamp screw and was measured using a load cell. The compression pressure was set at 1 MPa, which was similar to that measured in a typical PEFC. Air flow rates in the through-plane and in-plane direction of the GDL, as shown in Fig. 3, were measured using a mass flow meter. Maximum pore and mean flow pore diameters of GDLs were measured using through-plane permeability tests according to the ASTM standard test method for pore size characteristics [16]. A low surface tension ($\gamma = 0.0157 \text{ N m}^{-1}$) wetting liquid, Galwick [17], was used to wet the GDL and fill its pores. The dry flow curve that represented the relationship between the flow rate and the supplied air pressure was obtained with a completely dry GDL. The wet flow curve was obtained with a wetted GDL, in which a wetting liquid filled the pores of the GDL. The half-dry flow curve corresponded to one half the measured dry flow curve at a given air pressure.

By applying an air pressure across the wetted GDL, the liquid was displaced from the pores. The equilibrium relationship between the surface tension of the liquid and the air pressure, as shown in Fig. 4, was used to calculate the pore diameter;

$$d = \frac{4\gamma \cos \theta}{P} \quad (1)$$

where d was pore diameter, γ and θ were the surface tension and contact angle of the wetting liquid, respectively, and P was the air pressure acting on the liquid in the pore. The contact angle of the

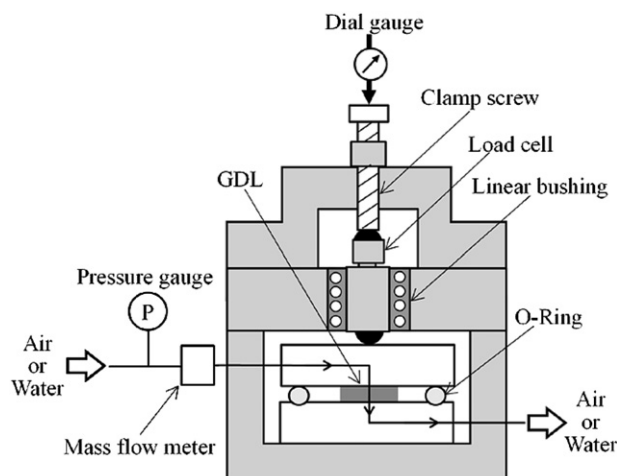


Fig. 2. Schematic diagram of air and water permeability test apparatus.

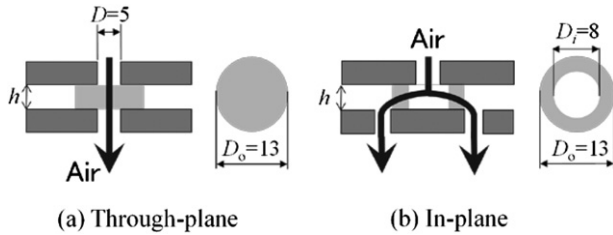


Fig. 3. Major dimensions of GDL used for through-plane and in-plane permeability tests.

wetting liquid was close to 0° . The minimum pressure at which air began to flow by clearing of the first pore was the maximum pore (bubble point) pressure, which was used to calculate the maximum pore diameter d_{\max} . The pressure was further increased and progressively smaller pores were cleared until the GDL was fully dried. The mean flow pore diameter d_m was calculated using the mean flow pressure that corresponded to the intersection of the wet flow and half-dry flow curves. The mean flow pore diameter of the hydrophobic intermediate MPL in the double MPL coated GDL could not be directly measured. Therefore, the mean flow pore diameter of the hydrophobic intermediate MPL just before coating the hydrophilic layer was measured.

The cross-sectional view of the MPL coated GDLs demonstrated that the MPL was not simply coated on the substrate surface, but penetrated deeply into the porous substrate [14]. Because the boundary between the MPL and the substrate observed from the micrograph was neither clear nor uniform, it was difficult to measure the MPL thickness considering the penetration into the substrate. Therefore, the average thickness of the MPL considering the penetration into the substrate was evaluated by a comparison of the measured in-plane permeability using GDLs with and without MPLs [14].

The hydrophobic and hydrophilic properties of the GDL are generally evaluated using the contact angle, which is commonly measured by the sessile drop method. However, because the contact angle measured using the sessile drop method is significantly dependent on the surface roughness of the GDL and the weight of the water droplet, it is difficult to accurately evaluate the contact angle. Therefore, a new technique was developed to measure the contact angle inside the GDL pore [14]. The water permeability test in the through-plane direction of the GDL was conducted using the same apparatus shown in Fig. 2. The minimum pressure at which water began to flow through the largest pore of the GDL was the maximum pore pressure. The maximum pore diameter was calculated using Eq. (1). The surface tension of water at 25°C was set at 0.0720 N m^{-1} [18]. When the maximum pore diameter measured using the water permeability test was assumed to be the same as that measured using the air permeability test, the contact angle inside the GDL pore could be accurately estimated.

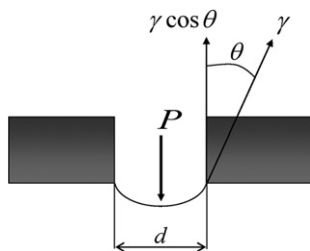


Fig. 4. Equilibrium relationship between the surface tension of the liquid and the air pressure.

The water vapor permeability was measured using a test apparatus, as shown in Fig. 5. The MPL coated GDL was sandwiched between two stainless-steel plates with a flow channel that was 1 mm wide, 40 mm long, and 1 mm deep. Dry air was supplied through the flow channel of the upper plate in contact with the carbon paper substrate. Liquid water was supplied at a pressure of 5 kPa through the flow channel of the lower plate in contact with the MPL. The water breakthrough pressure at which liquid water began to flow through the MPL was more than 15 kPa, which was higher than the supplied water pressure; therefore, the water vapor was transported through the MPL coated GDL to the air flow channel in the upper plate. The temperature of the two plates was set at 75°C . Under steady-state conditions, the water vapor flow rate through the MPL coated GDL was obtained from relative humidity (RH) measurements of the inlet and outlet air. The water vapor permeance q was defined as the water vapor flow rate divided by the permeable cross-sectional area of the GDL.

2.3. PEFC performance tests

PEFC performance tests under low and high humidity were conducted as follows. The cell temperature was set at 75°C . The active area of the MEA (GORE PRIMEA®5580) was 4.2 cm^2 . The separator had a triple serpentine flow channel configuration. Anode and cathode gases were supplied in a counter-flow orientation. Hydrogen and air utilization was set to 70 and 60%, respectively. For PEFC performance tests under low humidity, the relative humidity (RH) of the supplied gas at the cathode was set to 0%, while maintaining the gas supplied to the anode at 60% RH. For PEFC performance tests under high humidity, the RH of the gases supplied to both the anode and cathode was set to 100%.

IR (ohmic loss), activation and concentration overpotentials were measured separately as follows [14]. The anode overpotential (η_a) was obtained as the difference between the anode cell voltage and the reference hydrogen electrode. The open circuit voltage (OCV) overpotential (η_{OCV}) was measured as the potential drop between the Nernst potential (E_0) and the OCV. The IR overpotential (η_{IR}) was measured using the current-interruption method. The cathode concentration overpotential (η_{CC}) was determined by separating the voltage given by Tafel's equation from the cathode overpotential. The cathode activation overpotential (η_{CA}) was calculated by subtracting the above overpotentials and the output voltage (V_{eff}) from E_0 as follows:

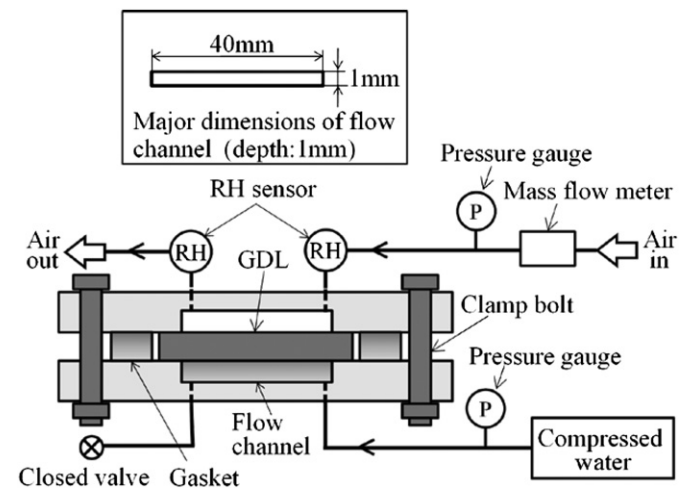


Fig. 5. Schematic diagram of water vapor permeability test apparatus.

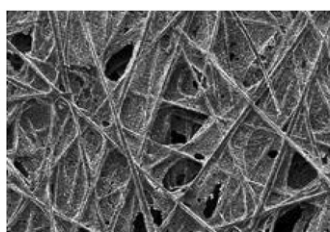
$$\eta_{CA} = E_0 - \eta_A - V_{eff} - \eta_{CC} - \eta_{OCV} - \eta_{IR} \quad (2)$$

There was no significant difference in the activation overpotentials obtained for all the hydrophilic and hydrophobic double MPL coated GDLs. Therefore, the influence of the double MPL coated GDLs on the IR and concentration overpotentials are discussed with the following test results.

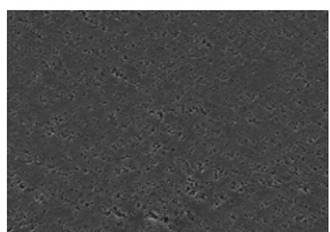
3. Results and discussion

3.1. Pore diameter, thickness and contact angle of the double MPL coated GDL

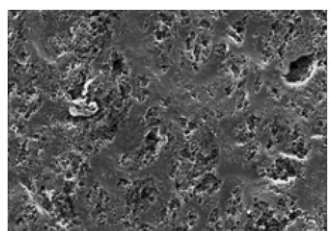
Figs. 6 and 7 show surface and cross-sectional scanning electron microscopy (SEM) micrographs of the GDLs with and without MPLs, respectively. The GDL substrate (SGL24BA) without an MPL had a mean flow pore diameter d_m of 42 μm . For the hydrophobic MPL coated GDL (SGL24BC), d_m of the hydrophobic MPL was 5 μm . For the double MPL coated GDLs, d_m of the hydrophilic layer was set at 5 μm . d_m of the hydrophobic intermediate MPL was controlled from 10 to 1 μm by reducing the water concentration in the MPL slurry from 89 to 76%. The average MPL thickness of the hydrophobic MPL coated GDL (SGL24BC) was



(a) GDL substrate (SGL24BA, $d_m=42\mu\text{m}$)

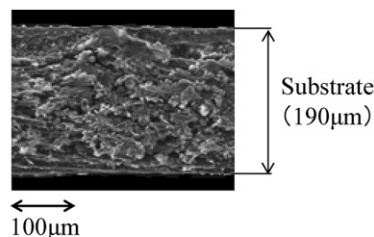


(b) Hydrophilic MPL in double MPL ($d_m=5\mu\text{m}$)

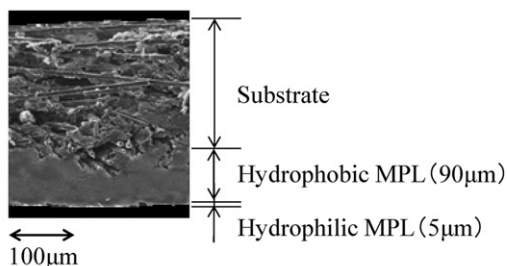


(c) Hydrophobic MPL in double MPL ($d_m=10\mu\text{m}$)

Fig. 6. Surface SEM micrographs of GDL with and without MPL.



(a) GDL substrate (SGL24BA, $h=190\mu\text{m}$)



(b) Hydrophilic and hydrophobic double MPL ($h=245\mu\text{m}$, $h_{PTFE}=90\mu\text{m}$)

Fig. 7. Cross-sectional SEM micrographs of GDL with and without MPL.

110 μm . The thickness of the hydrophobic intermediate MPL h_{PTFE} in the double MPL coated GDL was controlled between 90 and 170 μm by the clearance and pressure of the doctor blade in the coating machine. We have previously reported that the hydrophilic layer thickness for the double MPL coated GDL should be as small as possible to enhance the PEFC performance without an increase in the concentration overpotential [15]. Therefore, the hydrophilic layer thickness in the double MPL was set at 5 μm and the total thickness h of all double MPL coated GDLs was set at 245 μm .

Fig. 8 shows the contact angles obtained with the hydrophobic and the hydrophilic MPLs. The contact angle of the hydrophilic MPL using PVA was lower than that of the hydrophilic MPL using TiO_2 . An increase in the PVA content in the hydrophilic MPL from 5 to 10 mass% resulted in the enhanced hydrophilicity. When the PTFE content in the hydrophobic MPL was increased from 10 to 40 mass%, the hydrophobicity was enhanced, thereby increasing the contact angle.

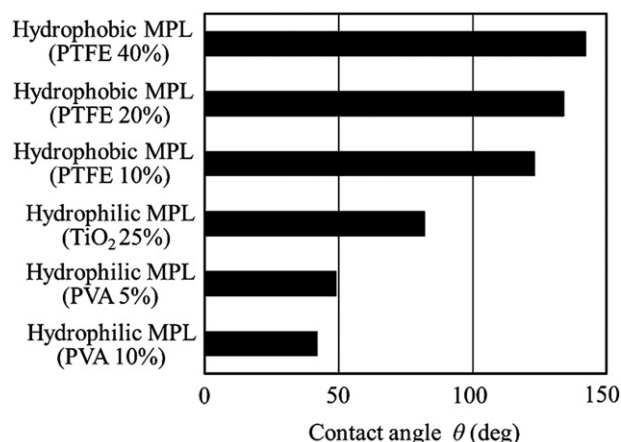


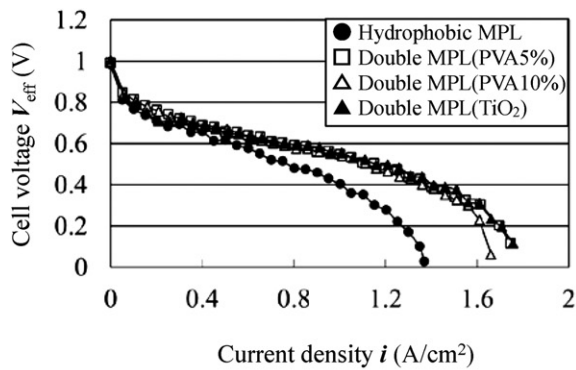
Fig. 8. Contact angles of hydrophobic MPLs and hydrophilic MPLs.

3.2. Influence of the hydrophilic layer in the double MPL coated GDL on the PEFC performance

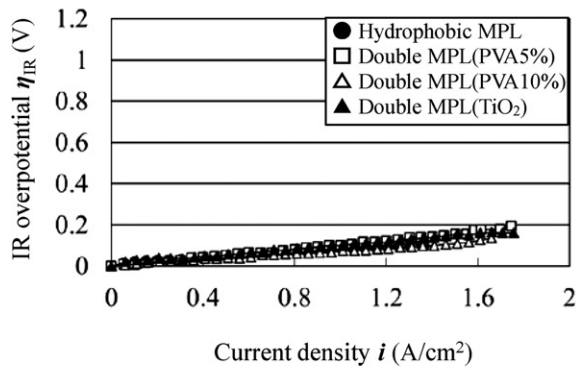
Fig. 9 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under low humidity (anode inlet gas: 60% RH, cathode inlet gas: 0% RH) with variation of the hydrophilicity of the hydrophilic layer. For the double MPL, the hydrophilic layers using 5 mass% PVA, 10 mass% PVA, and TiO_2 were tested. All hydrophilic layers were 5 μm thick with d_m of 5 μm . The parameters for the hydrophobic intermediate MPL were 20 mass% PTFE content, d_m of 3 μm , and h_{PTFE} of 90 μm . The reason for selecting this hydrophobic intermediate MPL is discussed later (see Sections 3.3–3.5). The SGL24BA GDL without the MPL, which was

effective at promoting water transport from the humidified anode gas to the MEA, was used at the anode [11].

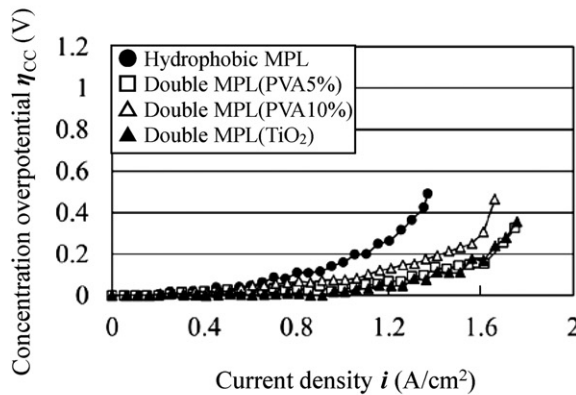
The PEFC performance obtained with all double MPL coated GDLs was higher than that with the hydrophobic MPL coated GDL (SGL24BC). The output voltages varied according to the hydrophilicity of the double MPL, although the IR overpotentials were relatively uniform for all double MPL coated GDLs. When the PVA content in the hydrophilic layer was higher, such as at 10 mass%, the PEFC performance tended to decrease. Excessive enhancement of the hydrophilicity resulted in an increase in water accumulated at the cathode catalyst layer, which reduced the diffusion of oxygen to the electrode and increased the concentration overpotential. However, appropriate hydrophilicity achieved by decreasing the



(a) Output voltage

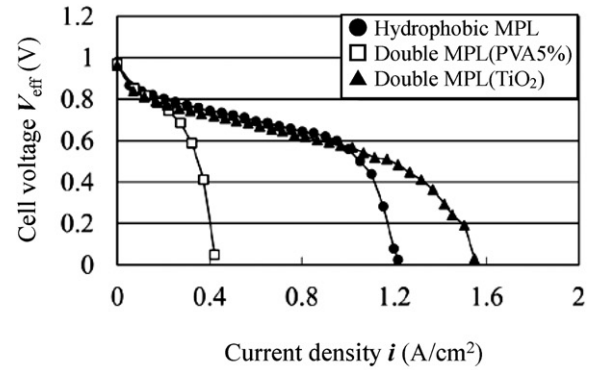


(b) IR overpotential

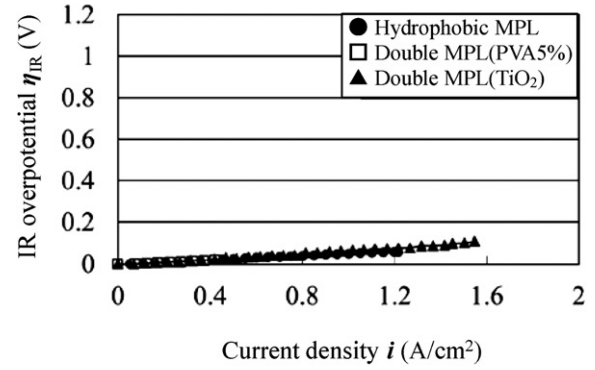


(c) Concentration overpotential

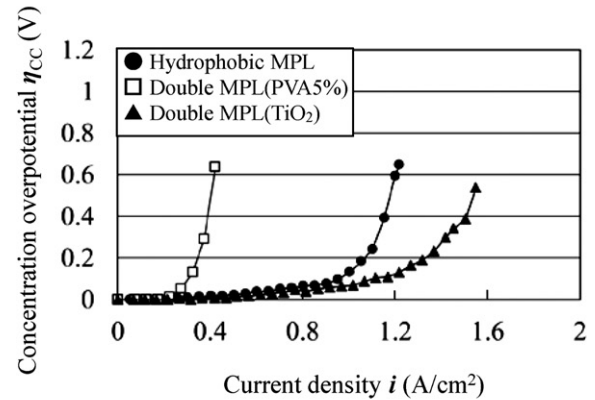
Fig. 9. Influence of hydrophilic layer in double MPL coated GDL (hydrophobic intermediate MPL: 20 mass% PTFE, $d_m = 3 \mu\text{m}$, $h_{\text{PTFE}} = 90 \mu\text{m}$) on PEFC performance under low humidity (anode: 60% RH, cathode: 0% RH).



(a) Output voltage



(b) IR overpotential



(c) Concentration overpotential

Fig. 10. Influence of hydrophilic layer in double MPL coated GDL (hydrophobic intermediate MPL: 20 mass% PTFE, $d_m = 3 \mu\text{m}$, $h_{\text{PTFE}} = 90 \mu\text{m}$) on PEFC performance under high humidity (anode: 100% RH, cathode: 100% RH).

PVA content to 5 mass% was effective for significant enhancement of the PEFC performance. Higher performance was also obtained with the hydrophilic layer using TiO_2 . The double MPL with a hydrophilic layer using either 5 mass% PVA or TiO_2 was effective at conserving the humidity of the MEA, while the hydrophobic intermediate MPL between the hydrophilic layer and the carbon paper substrate prevented the removal of water in the hydrophilic layer. This resulted in significant enhancement of the PEFC performance, compared with that for a conventional hydrophobic MPL coated GDL [15].

Fig. 10 shows the influence of the hydrophilicity of the double MPL coated GDL used at the cathode on the PEFC performance under high humidity (anode inlet gas: 100% RH, cathode inlet gas: 100% RH). The SGL24BA GDL without the MPL was used at the anode. Although the IR overpotentials were almost uniform for all the double MPL coated GDLs, the concentration overpotentials and the output voltages varied significantly according to the hydrophilic layer of the double MPL. The PEFC performance obtained with the hydrophilic layer using 5 mass% PVA was significantly degraded due to flooding; the hydrophilicity of the hydrophilic layer using PVA was too high under high humidity. This resulted in the accumulation of water at the catalyst layer, which reduced oxygen transport to the electrode and increased the concentration overpotential, thereby lowering the PEFC performance. However, the PEFC performance obtained with the hydrophilic layer using TiO_2 was enhanced and was much higher than that obtained with the hydrophobic MPL coated GDL.

These results indicate that an appropriate double MPL coated GDL using TiO_2 is effective at expelling excess water from the cathode catalyst layer to the carbon paper substrate. There was no significant difference in the air and liquid water permeability for the hydrophobic MPL and the double MPL coated GDLs measured using the permeability test apparatus shown in Fig. 2. The water vapor permeability was measured using the test apparatus shown in Fig. 5 to evaluate the ability of the MPL coated GDL to discharge water at the catalyst layer. Fig. 11 shows the variations in the water vapor permeance q with increase in the air velocity U for the hydrophobic MPL and the double MPL using TiO_2 . The air velocity was defined as the flow rate divided by the cross-sectional area of the air flow channel. The water vapor transport resistance at the GDL/air interface was significantly high under low velocity, which indicated the water vapor permeance of the MPL coated GDL was relatively low. As the air velocity was increased, the water vapor transport resistance at the GDL/air interface decreased, thereby increasing the water vapor permeance. The water vapor permeance obtained for the double MPL using TiO_2 was higher than that for the

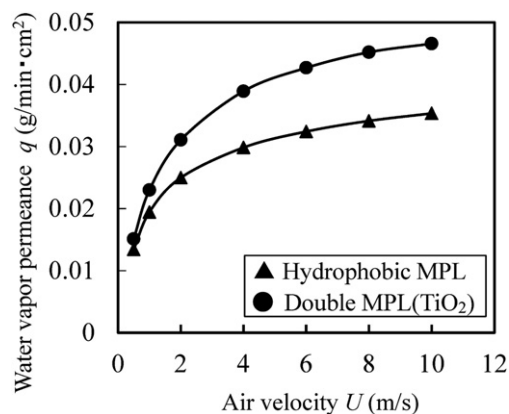


Fig. 11. Variations in water vapor permeance with increase in the air velocity for hydrophobic MPL and double MPL using TiO_2 (hydrophobic intermediate MPL: 20 mass% PTFE, $d_m = 3 \mu\text{m}$, $h_{\text{PTFE}} = 90 \mu\text{m}$).

hydrophobic MPL. It was difficult to introduce water into the small hydrophobic pores of the hydrophobic MPL coated GDL. However, the hydrophilic layer coated on the hydrophobic MPL of the double MPL was effective to promote the introduction of water into the small pores of the hydrophobic MPL, which resulted in the enhanced water vapor permeability of the double MPL, compared with that of the hydrophobic MPL.

A double MPL coated GDL with high water vapor permeability could be effective at enhancing discharge of excess water from the catalyst layer during PEFC operation under high humidity. Fig. 12 shows a schematic diagram that compares the water flow paths from the cathode catalyst layer to the carbon paper substrate obtained for the hydrophobic MPL and double MPL coated GDLs using TiO_2 . It is difficult for water droplets to be spread at the catalyst layer with the hydrophobic MPL coated GDL, which reduces the water flow paths through the hydrophobic MPL to the substrate. However, an appropriate double MPL coated GDL promotes water spreading at the catalyst layer, which increases the water flow paths to expel excess water from the catalyst layer to the substrate. This effectively reduced flooding at the catalyst layer, which enhanced the PEFC performance under high humidity, as shown in Fig. 10.

These results demonstrate that the double MPL coated GDL with the hydrophilic layer using TiO_2 is effective for enhancement of the PEFC performance under both low and high humidity, compared with that for a conventional hydrophobic MPL coated GDL. In the following sections, the influences of pore diameter, thickness and the hydrophobicity of the hydrophobic intermediate MPL on the PEFC performance are evaluated. For all double MPLs, a $5 \mu\text{m}$ thick hydrophilic layer using TiO_2 with d_m of $5 \mu\text{m}$ was coated on the hydrophobic MPL coated GDL.

3.3. Influence of the hydrophobic intermediate MPL pore diameter in the double MPL coated GDL on the PEFC performance

Fig. 13 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under low humidity with

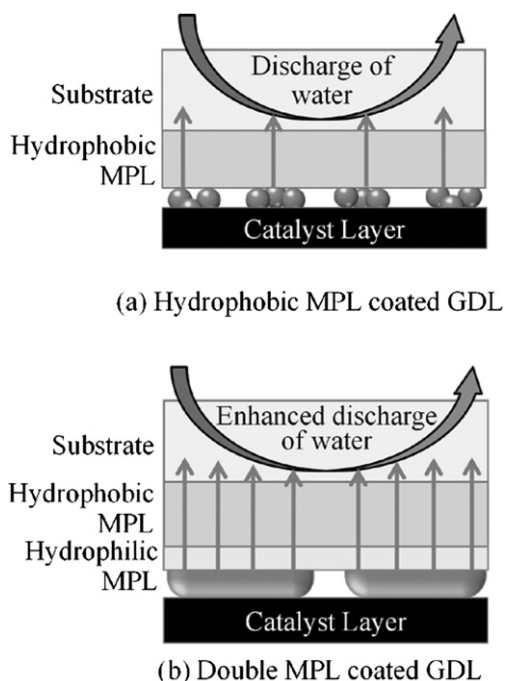
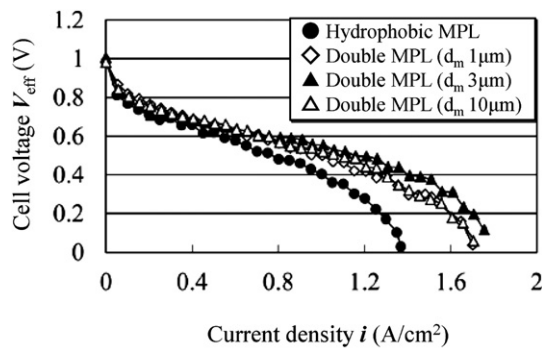


Fig. 12. Comparison of water flow paths from the catalyst layer to the substrate through the MPL for hydrophobic MPL and double MPL using TiO_2 .

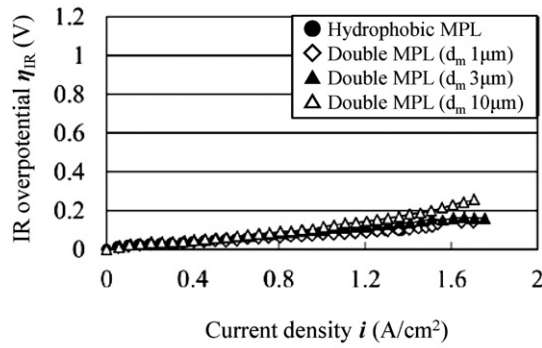
variation of the mean flow pore diameter d_m for the hydrophobic intermediate MPL (20 mass% PTFE, $h_{\text{PTFE}} = 90 \mu\text{m}$) between 1 and $10 \mu\text{m}$. The SGL24BA GDL without an MPL was used at the anode. The output voltages obtained for all double MPL coated GDLs were higher than that for the hydrophobic MPL coated GDL. The PEFC performance varied with the pore diameter of the hydrophobic intermediate MPL in the double MPL coated GDL. When the pore diameter was too large, such as at $10 \mu\text{m}$, the ability of the double MPL to prevent dehydration of the MEA was reduced, which resulted in an increase in the IR and concentration overpotentials, thereby lowering the PEFC performance. Decrease in the pore diameter to $3 \mu\text{m}$ reduced gas permeability, so that discharge of water in the hydrophilic layer to the substrate was difficult. This enhanced the ability of the double MPL to prevent dehydration of the MEA, which enhanced the PEFC performance significantly. However, when the pore diameter was too small, such as at $1 \mu\text{m}$,

the transport of excess water accumulated in the hydrophilic layer to the substrate was inhibited, which increased the concentration overpotential and lowered the PEFC performance.

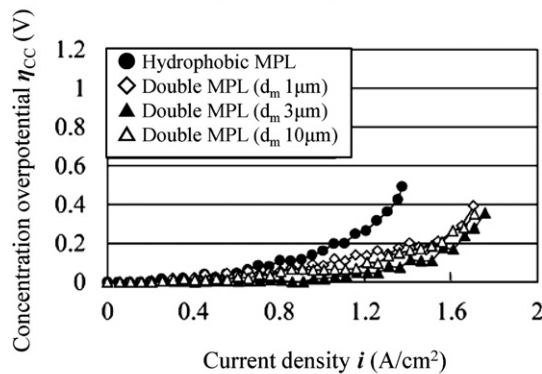
Fig. 14 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under high humidity with variation of d_m for the hydrophobic intermediate MPL between 1 and $10 \mu\text{m}$. The PEFC performance was more significantly varied with the pore diameter of the hydrophobic intermediate MPL than that under low humidity. Decrease in the pore diameter from 10 to $3 \mu\text{m}$ was effective to reduce flooding and achieve higher PEFC performance than that with the hydrophobic MPL coated GDL, due to the lower concentration overpotential, although the IR overpotential was relatively uniform for all the double MPL coated GDLs. However, when the pore diameter was too small, such as at $1 \mu\text{m}$, the PEFC performance was lower than that for the hydrophobic MPL coated GDL.



(a) Output voltage

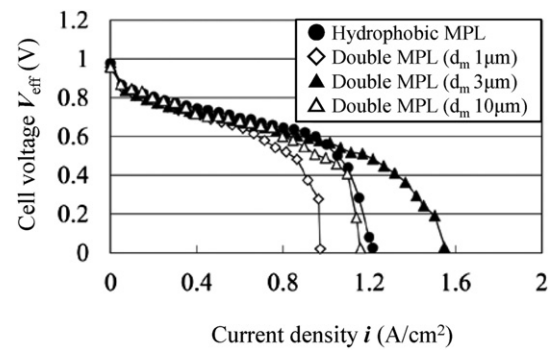


(b) IR overpotential

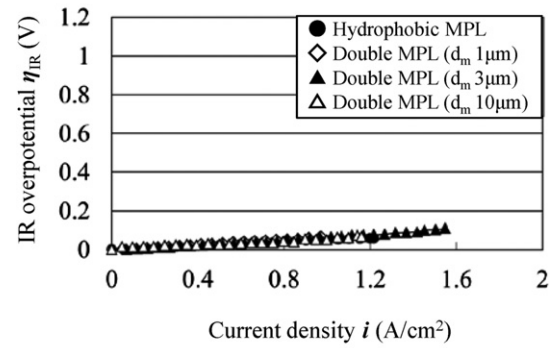


(c) Concentration overpotential

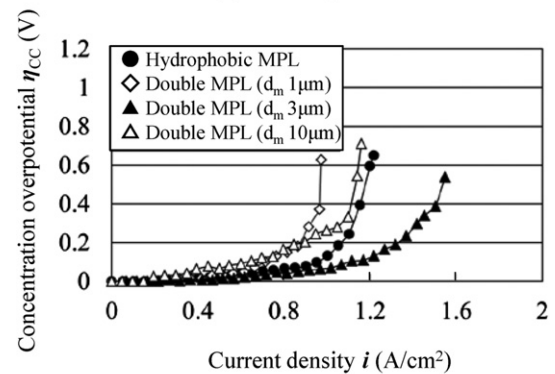
Fig. 13. Influence of hydrophobic MPL (20 mass% PTFE, $h_{\text{PTFE}} = 90 \mu\text{m}$) pore diameter in double MPL coated GDL on PEFC performance under low humidity (anode: 60% RH, cathode: 0% RH).



(a) Output voltage



(b) IR overpotential



(c) Concentration overpotential

Fig. 14. Influence of hydrophobic MPL (20 mass% PTFE, $h_{\text{PTFE}} = 90 \mu\text{m}$) pore diameter in double MPL coated GDL on PEFC performance under high humidity (anode: 100% RH, cathode: 100% RH).

The best performance was obtained with a hydrophobic intermediate MPL pore diameter of 3 μm , where excess water produced at the catalyst layer was expelled to the substrate through the double MPL and water droplets accumulated in a large portion of the pores in the substrate. An appropriate hydrophobic intermediate MPL was effective at preventing the back transport of water in the substrate to the hydrophilic layer, as shown in Fig. 15, so that most of the water accumulated in the substrate was expelled to the gas channel in the separator. This effectively prevented flooding at the cathode catalyst layer [14]. However, when the pore diameter was too large, such as at 10 μm , the water accumulated in the substrate was readily transported to the hydrophilic layer, which resulted in an increase in water accumulated at the catalyst layer. This promoted flooding, which significantly lowered the PEFC performance. When the pore diameter was too small, the transport of water accumulated in the hydrophilic layer to the substrate was inhibited and the diffusion of oxygen to the electrode was reduced. This resulted in a higher concentration overpotential, which lowered the PEFC performance compared with that for the hydrophobic MPL coated GDL.

3.4. Influence of the hydrophobic intermediate MPL thickness in the double MPL coated GDL on the PEFC performance

Fig. 16 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under low humidity with variation of the hydrophobic intermediate MPL (20 mass% PTFE, $d_m = 3 \mu\text{m}$) thickness h_{PTFE} between 90 and 170 μm . The output voltages obtained for all the double MPL coated GDLs were higher than that for the hydrophobic MPL coated GDL. The PEFC performance was varied with the hydrophobic MPL thickness; that obtained with a hydrophobic MPL thickness of less than 120 μm was higher than that with a hydrophobic MPL thickness of 170 μm . Increase in the hydrophobic layer thickness of the double MPL reduced gas permeability, which is advantageous to maintain the humidity of the MEA [14]. However, when the hydrophobic MPL thickness was too large, the transport of water accumulated in the hydrophilic layer to the substrate was difficult and oxygen transport to the electrode through the thick MPL was also inhibited, which increased the concentration overpotential and lowered the PEFC performance.

Fig. 17 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under high humidity with variation of h_{PTFE} between 90 and 170 μm . The PEFC performance varied more significantly with the hydrophobic MPL thickness than that under low humidity. A reduction in the hydrophobic MPL thickness to 90 μm increased the cross-sectional area of the porous substrate, which improved in-plane gas permeability [14]. This was effective at promoting the discharge of water accumulated in the

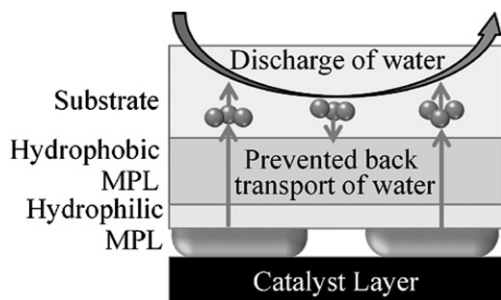


Fig. 15. Enhanced ability to prevent flooding for the double MPL with an appropriate hydrophobic intermediate MPL pore diameter ($d_m = 3 \mu\text{m}$).

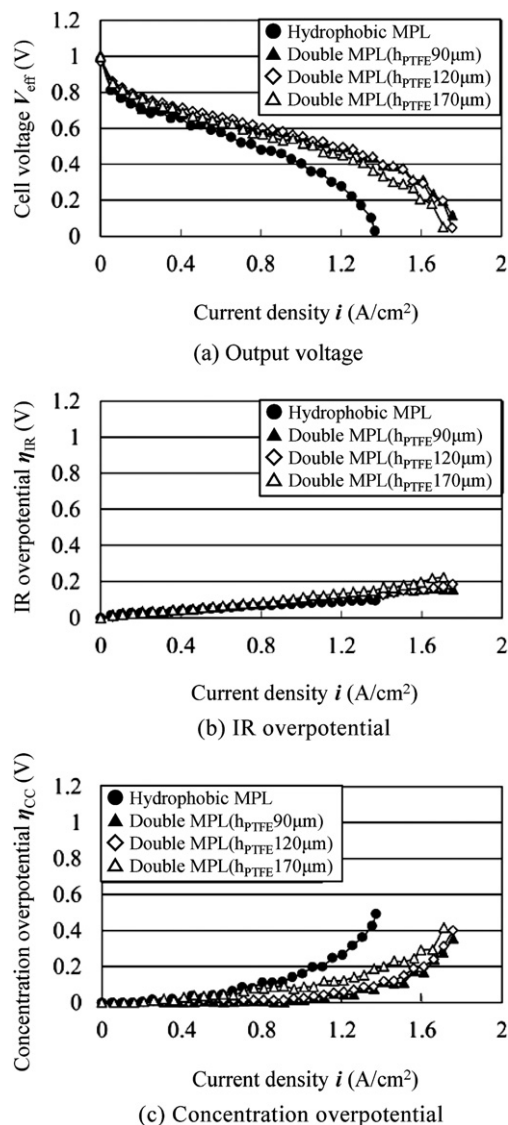


Fig. 16. Influence of hydrophobic MPL (20 mass% PTFE, $d_m = 3 \mu\text{m}$) thickness in double MPL coated GDL on PEFC performance under low humidity (anode: 60% RH, cathode: 0% RH).

substrate to the gas channel in the separator, thereby enhancing the ability of the double MPL to prevent flooding under high humidity. However, when the hydrophobic MPL thickness was increased, the discharge of water in the hydrophilic layer to the substrate through the MPL was difficult, which resulted in a higher concentration overpotential and lowered the PEFC performance, compared with that for the hydrophobic MPL coated GDL.

3.5. Influence of PTFE content in the hydrophobic intermediate MPL of the double MPL coated GDL on the PEFC performance

Fig. 18 shows the influence of the double MPL coated GDL used at the cathode on the PEFC performance under low humidity with variation of the PTFE content in the hydrophobic intermediate MPL ($d_m = 3 \mu\text{m}$, $h_{\text{PTFE}} = 90 \mu\text{m}$) between 10 and 40 mass%. The output voltages obtained for all the double MPL coated GDLs were higher than that for the hydrophobic MPL coated GDL. The influence of the pore diameter and thickness of the hydrophobic intermediate MPL on the PEFC performance under low humidity was relatively significant, as shown in Figs. 13 and 16. However, there was no

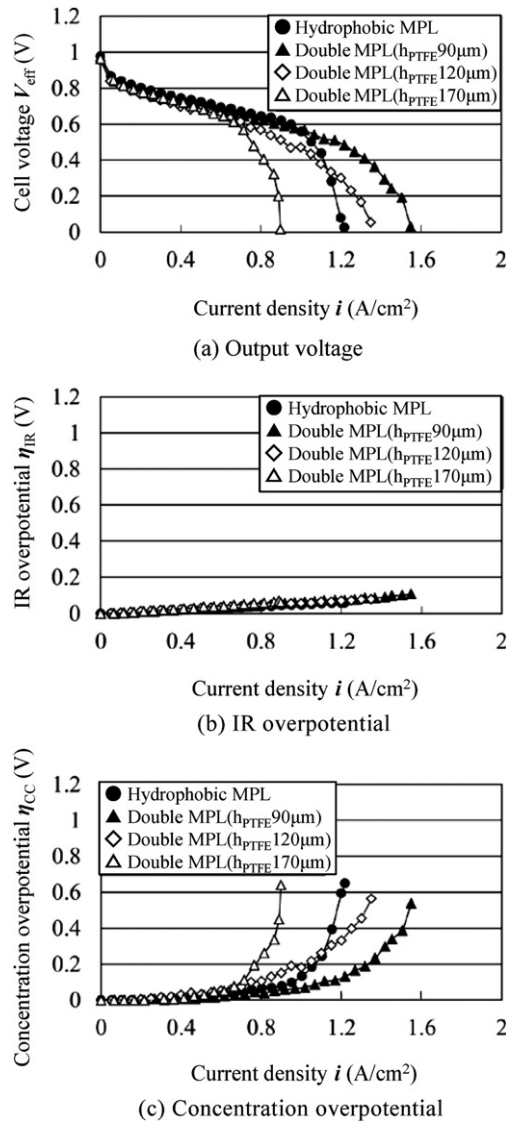


Fig. 17. Influence of hydrophobic MPL (20 mass% PTFE, $d_m = 3 \mu$ m) thickness in double MPL coated GDL on PEFC performance under high humidity (anode: 100% RH, cathode: 100% RH).

significant difference in the PEFC performance when the PTFE content in the hydrophobic intermediate MPL was varied between 10 and 40 mass%. Decrease in the PTFE content reduces the hydrophobicity of the single hydrophobic MPL coated GDL, which is advantageous to maintain the humidity of the MEA [14]. However, the hydrophilic layer in the double MPL coated GDL played an important role to conserve humidity at the catalyst layer; therefore, the hydrophobicity of the hydrophobic intermediate MPL was not a significant factor that influenced the ability of the double MPL to prevent dehydration of the MEA under conditions where the pore diameter and thickness of the hydrophobic intermediate MPL were the same.

Fig. 19 shows the influence of the double MPL coated GDL on the PEFC performance under high humidity with variation of the PTFE content in the hydrophobic intermediate MPL between 10 and 40 mass%. The PEFC performance obtained for the double MPL coated GDLs varied significantly with the PTFE content in the hydrophobic intermediate MPL, which is very different from that under low humidity. When the PTFE content was low, such as at 10 mass%, the hydrophobicity was insufficient for excess water in

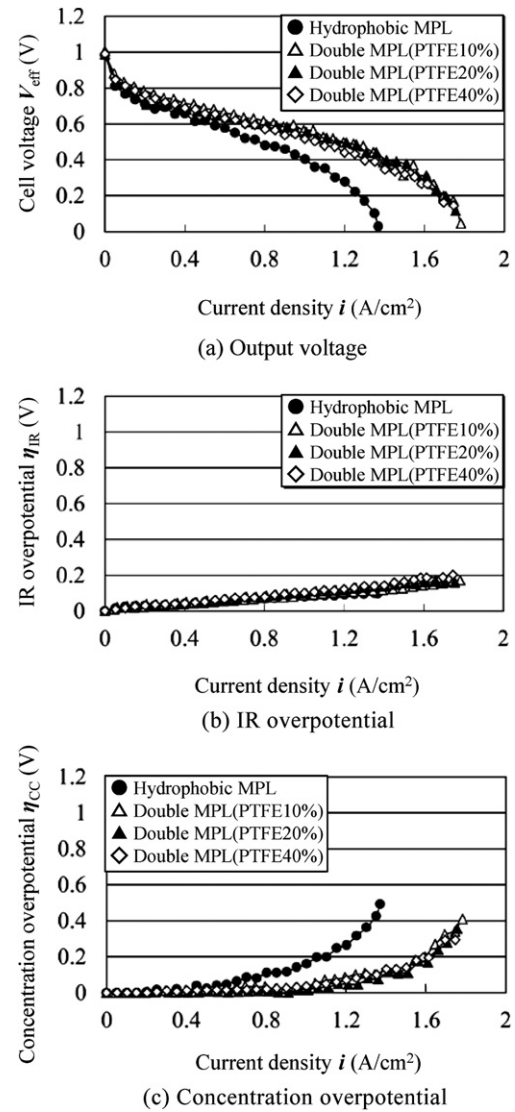


Fig. 18. Influence of PTFE content in hydrophobic MPL ($d_m = 3 \mu$ m, $h_{PTFE} = 90 \mu$ m) of double MPL coated GDL on PEFC performance under low humidity (anode: 60% RH, cathode: 0% RH).

the hydrophilic layer to be expelled to the substrate. This reduced the ability of the double MPL to prevent flooding, so that no significant enhancement in the PEFC performance could be expected. Increasing the PTFE content to 20 mass% enhanced the hydrophobicity of the intermediate MPL, which promoted the discharge of water in the hydrophilic layer to the substrate and effectively enhanced the ability of the double MPL to prevent flooding. However, when the PTFE content was increased to 40 mass%, the hydrophobicity of the intermediate MPL became too high, which resulted in a reduction of the water flow paths in the hydrophobic intermediate MPL for expelling excess water in the hydrophilic layer. This promoted flooding, which resulted in a lower PEFC performance than that obtained with the hydrophobic MPL coated GDL.

These results demonstrate that the pore diameter, thickness and the hydrophilic and hydrophobic properties of the double MPL coated GDL significantly influence the water management characteristics of PEFCs. Further study is required to accurately determine the mechanism concerning the water vapor, liquid water, and reactant gas transport properties inside the MPL coated GDL, and to further enhance the PEFC performance under both low and high humidity.

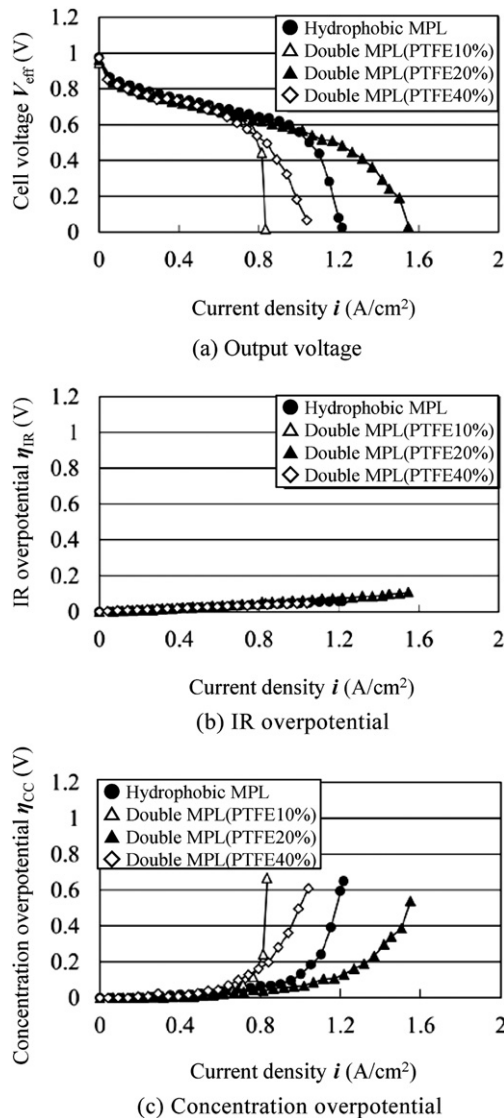


Fig. 19. Influence of PTFE content in hydrophobic MPL ($d_m = 3 \mu\text{m}$, $h_{\text{PTFE}} = 90 \mu\text{m}$) of double MPL coated GDL on PEFC performance under high humidity (anode: 100% RH, cathode: 100% RH).

4. Conclusions

A novel hydrophilic and hydrophobic double MPL coated GDL was developed to enhance PEFC performance under both low and high humidity. The influences of thickness, pore diameter, and the hydrophilic and hydrophobic properties of the double MPL on the PEFC performance were investigated. The following conclusions were obtained:

- (1) Hydrophilic layers using either PVA or TiO_2 in the double MPL coated GDL were effective at conserving the humidity of the MEA, while the hydrophobic intermediate MPL between the

hydrophilic layer and the carbon paper substrate prevented the removal of water from the hydrophilic layer. This further enhanced the PEFC performance under low humidity, compared with that for a conventional hydrophobic MPL coated GDL.

- (2) The hydrophilicity of the hydrophilic layer using PVA was too high, so that the PEFC performance under high humidity was significantly degraded due to flooding. The double MPL coated GDL with an appropriate hydrophilic layer using TiO_2 was effective at reducing flooding, which resulted in a higher PEFC performance than that for a conventional hydrophobic MPL coated GDL under both high and low humidity.
- (3) The PEFC performance under high humidity was more strongly dependent the design parameters of the hydrophobic intermediate MPL than that under low humidity. The best performance was obtained with a hydrophobic intermediate MPL pore diameter of $3 \mu\text{m}$. When the pore diameter was too low, the PEFC performance was degraded due to flooding. Appropriate enhancement of the hydrophobicity, which was achieved with 20 mass% PTFE content in the hydrophobic MPL, was essential for reducing flooding. Reducing the hydrophobic MPL thickness also enhanced the ability of the double MPL to prevent flooding.

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References

- [1] M. Mathias, J. Roth, J. Fleming, W. Lehnert, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), *Handbook of Fuel Cells – Fundamentals Technology and Applications*, vol. 3, John Wiley & Sons Ltd., England, 2003, pp. 456–463.
- [2] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, John Wiley & Sons Ltd., UK, 2003, pp. 75–90.
- [3] M. Hori, in: T. Honma (Ed.), *Handbook of Hydrogen and Fuel Cells*, Ohmsha Ltd., Japan, 2006, pp. 157–162.
- [4] M. Mench, *Fuel Cell Engines*, John Wiley & Sons Ltd., UK, 2008, pp. 295–298.
- [5] P. Corbo, F. Migliardini, O. Veneri, *Hydrogen Fuel Cells for Road Vehicles*, Springer-Verlag London Ltd., UK, 2011, pp. 116–128.
- [6] T. Kitahara, T. Konomi, H. Nakajima, Y. Seguchi, *Transactions of the Japan Society of Mechanical Engineers Series B* 76 (771) (2010) 1956–1963.
- [7] T. Kitahara, H. Nakajima, M. Morishita, *Journal of Power Sources* 214 (2012) 100–106.
- [8] Z. Qi, A. Kaufman, *Journal of Power Sources* 109 (2002) 38–46.
- [9] P.M. Wilde, M. Mändle, M. Murata, N. Berg, *Fuel Cells* 4 (3) (2004) 180–184.
- [10] J. Chen, T. Matsuura, M. Hori, *Journal of Power Sources* 131 (2004) 155–161.
- [11] T. Kitahara, T. Konomi, H. Nakajima, Y. Tateishi, M. Murata, N. Haak, P.M. Wilde, *ECS Transactions* 16 (2) (2008) 1603–1613.
- [12] T. Kitahara, T. Konomi, H. Nakajima, M. Murata, *Journal of Environment and Engineering* 4 (2) (2009) 338–345.
- [13] T. Sasabe, P. Deevanhxay, S. Tsushima, S. Hirai, *Journal of Power Sources* 196 (2011) 8197–8206.
- [14] T. Kitahara, T. Konomi, H. Nakajima, *Journal of Power Sources* 195 (2010) 2202–2211.
- [15] T. Kitahara, H. Nakajima, K. Mori, *Journal of Power Sources* 199 (2012) 29–36.
- [16] American Society for Testing and Materials Committee, ASTM, F316-86 (1970) 722–727.
- [17] A. Jena, K. Gupta, *Journal of Power Sources* 96 (2001) 214–219.
- [18] The Society of Chemical Engineers, Japan, *Chemical Engineering Handbook*, Maruzen, Japan, 2004, p. 96.